Experimental report

Proposal: 9-11-1984	**Council:** 4/2020

Title: Responsive air-water interfaces from polyelectrolytes and photo-switchable surfactant mixtures

Research area: Chemistry

This proposal is a new proposal

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Samples: Poly(diallyldimethylammonium chloride)
butyl-arylazopyrole sulfonate
Arylazopyrazole triethylammonium bromide
sodium polystyrole sulfonate

Instrument	Requested days	Allocated days	From	To
FIGARO Adsorption troughs	3	3	29/01/2021	01/02/2021

Abstract:

This new proposal concerns the use of photo-switchable surfactants in oppositely charged P/S mixtures as a means to control the interfacial behavior of P/S systems for the first time. In previous work it has not been possible to tune the interactions between the polyelectrolyte and the surfactant using an external stimulus. Although electrostatic interactions dominate the P/S interaction, dispersive interactions are also relevant and can substantially shift the chemical potential for P/S binding. Using photo-switchable surfactants we are now able to modulate dispersive interaction and thus P/S binding by mak-ing use of the remote E to Z photo isomerization of the surfactants. We propose to perform neutron reflectometry experiments with photo-switchable P/S mixtures in order to obtain structural and compo-sition information both at equilibrium and during photo-switching that is otherwise inaccessible. FIGARO has the flux at low Q that can allow us to deliver us a full structural, compositional and kinet-ic study of these systems.

Preliminary Experiment Report: Responsive air-water interfaces from polyelectrolytes and photo-switchable surfactant mixtures (#9-11-1984)

Introduction

Active surfaces and interfaces which can respond to external stimuli such as light or temperature and can change their chemistry on demand have great potential to serve as hierarchical elements for responsive functional materials such as foams. In experiment #9-11-1984 we have now addressed mixtures of photo-switchable arylazopyrazole (AAP) surfactants with two polymers the anionic polyelectrolyte sodium polystyrene sulfonate (PSS) and the cationic polyelectrolyte polydiallyldimethyl ammonium chloride (PDADMAC). The 2 surfactants which were used in this experiment have been studied without the presence of polyelectrolytes in previous FIGARO experiments using neutron reflectivity (NR) and were also studied with complementary experiments with sum-frequency generation (SFG) spectroscopy. The results on the behavior of the anionic surfactant butyl-arylazopyrazole sulfonate (butyl-AAP-C$_4$S) and the cationic photo-switchable surfactant arylazopyrazole triethylammonium bromide (AAP-TB) were published elsewhere.[1,2] Both surfactants can undergo E/Z photo-isomerization reactions when irradiated with 520 nm (green) light (Z→E) and 365 nm (UV) light (E→Z) which is used to change their surface excess and structure remotely. In particular, for butyl-AAP-C$_4$S previous NR and SFG experiments have suggested that a monolayer to bilayer transition can take place, which is discussed in detail elsewhere.[1]
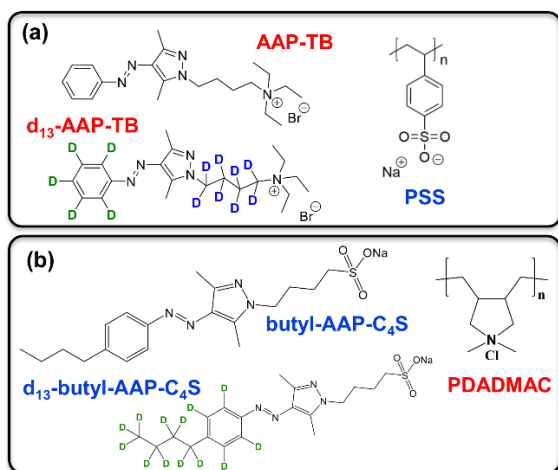

Fig. 1 Molecular structure of the polyelectrolyte/surfactant systems that were investigated: (a) AAP-TB with PSS and (b) PDADMAC/butyl-AAP. Also shown the deuterated analogues.

In experiment # 9-11-1984, we have studied two responsive systems PDADMAC/butyl-AAP-C$_4$S as well as PSS/AAP-TB mixtures. The chemical structure of the molecules that were used in the experiment are shown in Fig. 1. Note that for both systems we have additionally synthesized partially deuterated forms of the new surfactants to be able to resolve the surface excess and interfacial structure of the surfactants and polyelectrolytes. This can be used to qualitatively determine the interfacial charging state and can be compared to the information from SFG spectroscopy which also provide a qualitative measure of interfacial charging as was previous reported.[3] In addition, the bulk aggregation/ particle formation was studied using dynamic light scattering (DLS) and by addressing the electrophoretic mobility. These results can be qualitatively compared to the interfacial structure as a function of P/S mixing ratio. Clearly, application of photo-switchable surfactants allows us to change bulk and interfacial properties such as composition and the interfacial charging state remotely by light irradiation (UV vs green light). It was the aim of experiment #9-11-1984 to obtain structural and composition information on air-water interfaces decorated with the P/S mixtures shown in Figs. 1a and b.

Experimental Details

The beam time of #9-11-1984 was performed under severe restrictions imposed by the Covid-19 pandemic and could only be performed as a remote experiment with a limited number of team members on site. *We kindly thank Javier Carrascosa Tejedor, Samuel Winnall and Philipp Gutfreund for their work!* This forced us to adjust the number of sample changes so that they could be still handed by the reduced crew on site during the experiment. For that reason, we could not study as many concentrations to reveal the adsorption isotherms of the mixtures as we had originally planned. The time was instead used to study concentrations that require relatively long adsorption times.

To address the aims of the experiments we have studied both systems in *3 isotopic contrasts*: h- and d-surfactants in air contrast matched water (ACMW) and d-surfactants in D$_2$O. The planned contrast of h-surfactant in D$_2$O was dropped because we could only plan 3 long structural measurements instead of 4 due to the restrictions outlined above. For each system, we have kept the surfactant concentration constant at 1 mM butyl-AAP-C$_4$S and 7 mM AAP-TB that are close to the maximum changes at the air-water interface in the absence of a polyelectrolyte (i.e. surfactant only) during photo-switching. These concentrations can be well justified and are based on our published work[1,2] where we have applied NR and SFG spectroscopy to study the composition and structure of air-water interfaces that were decorated with only AAP-TB or butyl-AAP-C$_4$S surfactants.

For experiment #9-11-1984, first the 6-position sample changer adapted to contain both green and UV LEDs (as was done in our previous experiments) was set up. Direct beams and pure solvent calibrations were run for a total of 6 h. A delay to the experiment of over 24 h was experienced due to a problem with an electronic update to the detector, but we were offered almost all the missing time at the end of the experiment in compensation.

Structural Data Analysis

We conduced structural measurements using the full Q-range for each system: PDADMAC/butyl-AAP and PSS/AAP-TB. These were done at 3 selected concentrations and in 3 isotopic contrasts. For the PSS/AAP-TB system we recorded the full Q-range for P:S molar ratios of 1:2, 1:5 and 1:120, while for the PDADMAC/butyl-AAP-C$_4$S system the full Q-range was recorded for 1:1, 1:2 and 1:100. The P:S ratios correspond to zero net charge in the two-phase region, excess polyelectrolyte and excess surfactant. Each structural measurement allowed for sufficient adsorption time (90 to 180 min) under green or UV irradiation and included the structural measurement over the full Q-range under continuous light irradiation as well as a second waiting time until the samples had reached a new equilibrium after the irradiation and therefore the E/Z conformation of the surfactants was switched. Once equilibrium was reached, the full Q-range was recorded again. This resulted in two sets of structural data where the surfactants are either in the E (green) or the Z (UV) state and which causes different hydrophobic interactions and different polymer-surfactant binding as we will show below.

The structural data for the PSS/AAP-TB system fitted well to a layer of surfactant with polyelectrolyte under the headgroups, the amount of which depended on the molar mixing ratio. However, the data could be fitted well only when an upturn at low-Q that is characteristic of embedded aggregates in the film was removed. This was consistent with the presence of off-specular scattering, as is inferred from more recent work by Tummino et al.[4] We will surely benefit from the expertise of Philipp Gutfreund to exploit an off-specular analysis of these data, but the specular structural data are now fully fitted and ready to be included in a well-developed manuscript. Final fitting results are presented in fig. 2.
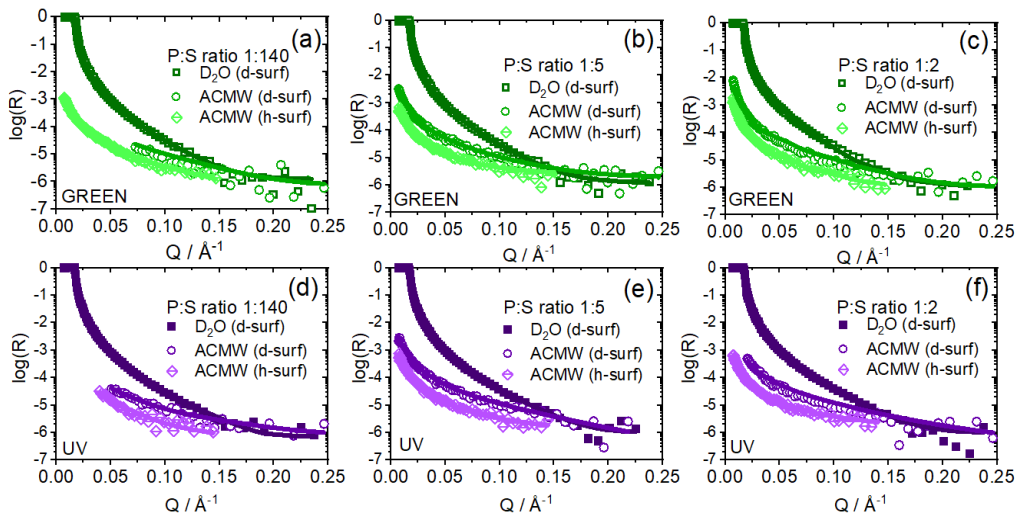

Fig. 2 *Reflectivity profiles for the PSS/AAP-TB mixtures in different contrasts (air-D$_2$O, air-ACMW) as well as for the deuterated (d-surf) and the hydrogenous (h-surf) surfactant (structures in Fig. 1). (a) – (f) present different mixing ratios and light irradiation as indicated in the figures. Solid lines are optimized model fits. Parameters in Table 1.*

As expected from the previous work of Staples et al.,[5] all measurements of the PDADMAC/surfactant systems fitted to a compact stratified layer model: layer 1 with acyl chains, layer 2 with solvated head groups and polyelectrolyte, and layer 3 with solvated polyelectrolyte. Preliminary fitting results are presented in fig. 3 with the fitting parameters listed in table1.
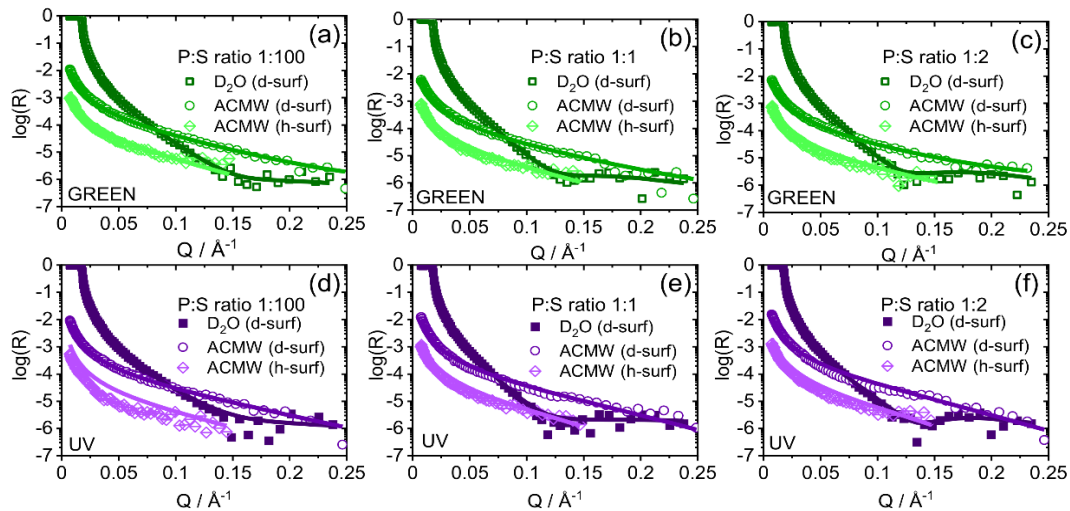

Fig. 3 *Reflectivity profiles for the PDADMAC/butyl-AAP mixtures in different contrasts (air-D$_2$O, air-ACMW) as well as for the deuterated (d-surf) and the hydrogenous (h-surf) surfactant (structures in Fig. 1). (a) – (f) present different mixing ratios and light irradiation as indicated in the figures. Solid lines are optimized model fits. Parameters in Table 1.*

P:S ratio	U_ζ / 10^{-8} m²/(Vs)	Γ_S / µmol/m²	Γ_P / µmol/m²	Chain-Layer Thickness / Å	Head-Layer-Thickness / Å	% P Head Layer	3rd layer thickness / Å	3rd layer % solvent
1:1	-1.7	3.5	4.3	10.7	9	40	11.5	85.3
1:1	3.5	4.3	4.6	13	9	47,5	21.3	93.7
1:2	-3.5	3.7	3.6	11.2	7	10	4.6	19.6
1:2	2.7	4.8	4.6	14.6	9	42	41.1	95.5
1:100	-1.5	4.5	1.6	13.5	7	20	2.9	82.1
1:100	0.3	3.8	1.4	11.4	8	10	1.8	46.0

Table 1 *Electrophoretic mobility (U_ζ) and surface excess of surfactant Γ_S and PDADMAC Γ_P from the full-Q fits presented in Fig. 2. In addition, structure information on the layer thickness as well as solvent mixing in the 3rd layer is presented.*

Compositional Data Analysis

In addition to the 36 sets of full-Q structural data (2 systems, 3 compositions, 3 contrasts, 2 illuminations), we have recorded NR data in the low-Q range to construct adsorption isotherms for the PDADMAC/ butyl-AAP-C4S and PSS/AAP-TB systems. Each mixing ratio was measured in two contrasts (h- and d-surfactants in ACMW) under green and UV irradiation following the recently developed low-Q compositional analysis approach. We studied 4 additional molar ratios for the PSS/AAP-TB mixtures (1:1000, 1:50, 1:2, 1:5, 2:1) and 2 additional molar ratios for the PDADMAC/butyl-AAP-C₄S (1:20, 1:10) mixtures. These experiments included a kinetic series making use of the high flux at FIGARO after sample loading and/or switching the light irradiation from 90 to 450 min adsorption time. Indeed, samples were loaded according to which ones were expected to equilibrate faster or more slowly in order to ensure that use of the beam time was optimized. It may be noted also that the low-Q analysis was conducted over the Q-range 0.022–0.034 Å⁻¹ rather than the standard 0.01–0.03 Å⁻¹ to minimize any influence of trapped aggregates in the films which cause an upturn in the data at very low Q.

The results are shown in fig. 4. Unfortunately, there are significant problems associated with the analysis, as the polyelectrolyte surface excesses are close to zero for the PSS system and strongly negative for the PDADMAC system. It may be the case that mixing of the surfactant headgroups (which have a slightly negative scattering length density) and polyelectrolyte (having a positive scattering length density) is making a proportion of the polyelectrolyte effectively invisible in the analysis. However, this cannot account for the strongly negative values of the polyelectrolyte surface excess in the PDADMAC system. A hint at the origin of the problem can be seen in fig. 2 where the model fits to the h-surf/ACMW contrast is above the data in every case, and significantly so in fig. 2d. This means that the low-Q analysis would need to add a negative amount of polymer for the model to fit the data, which explains the values in fig. 3b. Another issue could be that the scattering length density is between 0.13–0.59 x 10⁻⁶ Å⁻² depending on the degree of counterion association, which is unknown. It follows therefore that the systems involving d-surf and h-surf are not producing chemically identical interfaces, which is prerequisite of the analysis.
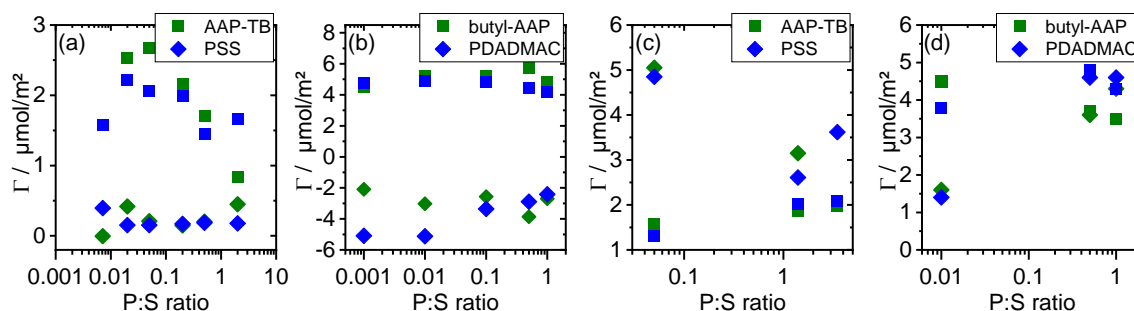

Fig. 4 *Calculated surface excess from the low-Q analysis for the two P/S surfactant mixtures as a function of the P:S mixing ratio for (a) PSS/AAP-TB and (b) PDADMAC/butyl-AAP mixtures. (c) and (d) shows the surface excess for PSS/AAP-TB and PDADMAC/butyl-AAP mixtures from the full-Q analysis (see also Tab. 1 and main text). Squares and diamond symbols indicate AAP and the polymer surface excess, while green and blue colored symbols indicate irradiation with green and UV light.*

Thankfully, the full-Q structural analysis approach did produce physically sensible values of the interfacial composition as shown in Fig. 2c and Tab. 1. Therefore, to go ahead and complete the data analysis for this system, and produce an isotherm that can be published, it will be necessary to record additional data over the full Q-range for the two contrasts PDADMAC/d-surf in ACMW and D₂O. It may seem surprising initially that these 2 contrasts will be sufficient to resolve the interfacial composition, but for a compact layer structure that is formed by PDADMAC,[4] these two contrasts are sufficient as the chains thickness is determined from the amount of surfactant in the surface monolayer in the ACMW data, and the amount and extension of the polyelectrolyte is determined by the fall-off of the D₂O data. It should be noted that due to expected non-monotonic changes in the interfacial composition,[6] we would not be comfortable to publish the results with just three resolved values of the interfacial composition.

References

1. C. Honnigfort et al. *Chem. Sci.* **2020**, *11*, 2085. // 2. M. Schnurbus et al. *J. Phys. Chem. B* **2020**, *124*, 6913. // 3. N. García Rey et al. *J. Phys. Chem. C* **2019**, *123*, 1279. // 4. A. Tummino et al. *Langmuir* **2018**, *34*, 2312. // 5. E. Staples et al. *Langmuir* **2002**, *18*, 5147. // 6. M. Uhlig et al. *Chem. Commun.* **2020**, *56*, 952.